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Jiro IRIYAMA, et al.

Japanese Patent Application No. 241916/1998

Japanese Patent Filing Date: August 27, 1998

for: "Nonaqueous Electrolyte Secondary Battery, Manufacturing Method Thereof, and Carbon Material Composition"

VERIFICATION OF TRANSLATION

Honorable Commissioner of Patents and Trademarks

Washington, D.C. 20231

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- (1) that he knows well both the Japanese and English languages;
- (2) that he translated the above-identified U.S. Application from Japanese to English;
- (3) that the attached English translation is a true and correct translation of the above-identified Japanese Application to the best of his knowledge and belief; and
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[Title of the Invention] Nonaqueous Electrolyte secondary battery, Manufacturing Method Thereof, and Carbon Material Composition

5 [Claims]

[Claim 1] A rechargeable nonaqueous electrolyte secondary battery comprising a positive electrode which can be doped with lithium ions and de-doped of lithium ions, a nonaqueous electrolyte solution and a negative electrode, wherein a negative
10 electrode active material consists essentially of a carbon material including at least a graphite material whose surface is covered with amorphous carbon and flake graphite particles.

[Claim 2] The nonaqueous electrolyte secondary battery according to claim 1, wherein a ratio of said flake graphite
15 particles is within a range of 10 to 70 wt% of all the carbon materials.

[Claim 3] The nonaqueous electrolyte secondary battery according to claim 1 or 2, wherein the specific surface area of said graphite material whose surface is covered with amorphous
20 carbon is within a range of 0.3 m²/g to 3 m²/g.

[Claim 4] The nonaqueous electrolyte secondary battery according to claim 3, wherein said graphite material whose surface is covered with amorphous carbon is obtained by graphitizing mesocarbon microbeads.

25 [Claim 5] The nonaqueous electrolyte secondary battery

according to any of claims 1 to 4, wherein a weight average particle diameter of said flake graphite particles is within a range of 10 μm to 80 μm .

[Claim 6] The nonaqueous electrolyte secondary battery
5 according to claim 5, wherein said flake graphite particles are artificial graphite obtained from petroleum pitch or coal pitch as a raw material.

[Claim 7] The nonaqueous electrolyte secondary battery
according to any of claims 1 to 6, wherein said carbon material
10 consists solely of graphite material whose surface is covered with amorphous carbon and said flake graphite particles.

[Claim 8] A method for manufacturing a nonaqueous electrolyte secondary battery, said method comprising steps of:

applying a slurry onto a current collector; the slurry
15 comprising a graphite material whose surface is covered with amorphous carbon, flake graphite particles and a binder in a dispersion medium;

drying the slurry; and

compressing the dried slurry by the application of a
20 pressure.

[Detailed Description of the Invention]

[Field of the Invention]

The present invention relates to a high-performance nonaqueous electrolyte secondary battery using an organic solvent
25 as an electrolyte solution, and more particularly, it relates

to a negative electrode material for a lithium ion secondary battery.

[Prior Art]

In recent years, as a power supply of a portable electronic device, demands for a secondary battery having a high energy density and excellent charge and discharge cycle properties are increasing. In this regard, the nonaqueous electrolyte secondary battery, especially a lithium ion secondary battery is very expected as a battery having a high voltage and a high energy density.

In particular, much attention has been nowadays paid to a battery system using a lithium-containing transition metal oxide as a positive electrode active material and a carbonaceous material as a negative electrode. For both positive and negative electrodes of this battery, there is utilized a mechanism of lithium ion intercalation, deintercalation, lithium ion doping or de-doping with respect to each active material, and hence, no metal lithium dendrite is formed even if the charge and discharge cycles are repeated, in contrast to a battery using metal lithium. This battery is, therefore, expected to exert the excellent charge and discharge cycle properties and safety.

At present, a carbon material is widely used as a negative electrode material for such a nonaqueous electrolyte secondary battery. As a proposal of using the carbon material as the negative electrode material, each of Japanese Patent Applications

Laid-Open Nos. 208079/1982, 102464/1983, 192266/1983,
143280/1984 and 54181/1985 discloses the employment of, e.g.,
graphite as the negative electrode material. However, the
crystallite of graphite is in the extremely developed state, and
5 so, in the nonaqueous electrolyte secondary battery using such
a negative electrode, the decomposition of the electrolyte
solution is apt to occur as a side reaction at the hexagonal mesh
surface ends of graphite crystals during charge, so that there
is a problem that a charge and discharge efficiency and the charge
10 and discharge cycle properties are poor.

In order to solve such a problem, there has been proposed
the use of a carbon material which has a low graphitization degree
and whose crystallite is not in the extremely developed state.
Specifically, it has been suggested that the graphitization degree
15 can be controlled by a calcination temperature, and a method using,
as the negative electrode, a calcined organic material obtained
at a calcination temperature of not more than 1500°C is disclosed
in Japanese Patent Applications Laid-Open Nos. 93176/1993 and
235372/1985. In such a carbon material having the low
20 graphitization degree, the decomposition of the electrolyte
solution during charge can be more suppressed as compared with
a carbon material calcined at a temperature not less than 2800°
C and having the high graphitization degree.

The carbon material having the low graphitization degree
25 has, however, lower charge and discharge efficiency than the

material having the high graphitization degree, and its true density is also low. Therefore, the obtained battery energy density becomes low, which is insufficient as a battery capacity.

Accordingly, each of Japanese Patent Applications
5 Laid-Open Nos. 059703/1998, 343196/1996, 368778/1992 and
66404/1992 discloses an attempt to suppress the side reaction
such as decomposition of the electrolyte solution to thereby
improve the battery properties by coating the surface of the carbon
material with amorphous carbon or carbonaceous decomposition
10 components to reduce the surface area of the carbon material or
covering the hexagonal mesh surface end of the active graphite
crystal.

Further, Japanese Patent Application Laid-Open No.
2428905/1993 discloses an attempt to suppress the side reaction
15 such as decomposition of the electrolyte solution to thereby
improve the battery properties by restricting a ratio of particles
which have a small particle diameter to reduce the surface area
of the graphite material.

When using the graphite material to a negative electrode
20 of the nonaqueous electrolyte secondary battery, since a main
cause of the irreversible capacity of the battery is the
decomposition reaction of the electrolyte solution which occurs
at the edge surface of the graphite crystal during charge, reducing
the surface area of the negative electrode material or covering
25 the material surface with the electrolyte solution and the

inactive coating film are effective for improving the charge and discharge efficiency.

[Problem to be Solved by the Invention]

In general, as a technique for working the carbon particles into an electrode, there is widely used a method which comprises mixing the carbon particles with a binder, dispersing the resultant mixture in an aqueous or organic solvent to obtain a slurry, applying this slurry on a current collector, and then drying the same. The negative electrode manufactured by this method has, however, a high void ratio and small filling density as it is, and hence the energy density of the battery can not be sufficiently increased.

In particular, since the material from which the carbon particles having a small particle diameter are removed for reducing the specific surface area has inferior filling properties, it is hard to increase the electrode density. Therefore, the electrode manufactured by the above-described method is usually compressed by using a roll press machine or a uniaxial press machine in order to increase the filling density.

In case of manufacturing the electrode by using the conventional carbon material, however, when the electrode is tried to be compressed in the manufacturing process, the improvement effect is decreased and the charge and discharge efficiency becomes lower. Thus, the battery in which such a carbon material is used for the electrode can not be compressed to sufficiently

increase the filling density of the electrode, and the energy density of the battery becomes lower, which leads to the insufficient battery capacity.

The present inventor has discovered that the reason for
5 the fact that the charge and discharge efficiency lowers by pressure compression of the electrode is due to the increase in the specific surface area of the electrode. Since compressing the electrode decreases the void ratio of the electrode, the surface area of the electrode is seemingly reduced. However,
10 when the electrode is compressed to, the specific surface area of the electrode is surprisingly greatly increased.

That is because compressing the electrode causes the carbon particles to be fragmentized. When the carbon particles are fragmentized, the specific surface area of the electrode is
15 increased, which readily provokes decomposition reaction of the electrolyte solution, thereby lowering the charge and discharge efficiency. Further, in case of the graphite material having the surface covered with amorphous carbon, when the carbon particles are fragmentized, the active carbon hexagonal mesh
20 surface edge which is not covered with amorphous carbon is exposed, and the effect obtained by coating is thus reduced. Therefore, deterioration of the charge and discharge efficiency due to compression becomes prominent.

In view of the above-described problems, it is an object
25 of the present invention to provide a high-performance nonaqueous

electrolyte secondary battery having the excellent charge and discharge efficiency.

[Means for Solving the Problem]

5 The present invention is directed to a rechargeable nonaqueous electrolyte secondary battery comprising a positive electrode which can be doped with lithium ions and de-doped of lithium ions, a nonaqueous electrolyte solution and a negative electrode, wherein a negative electrode active material consists
10 essentially of a carbon material (which may be referred to as a "negative electrode carbon material" for clarification hereinafter) including at least a graphite material whose surface is covered with amorphous carbon and flake graphite particles.

 Moreover, the present invention is also directed to a
15 method for manufacturing a nonaqueous electrolyte secondary battery, said method comprising steps of: applying a slurry onto a current collector; the slurry comprising a graphite material whose surface is covered with amorphous carbon, flake graphite particles and a binder in a dispersion medium; drying the slurry;
20 and compressing the dried slurry by the application of a pressure.

 According to examination by the present inventor, as described above, in case of manufacturing a negative electrode by using the covered graphite material as a negative electrode active material, when the negative electrode active material is
25 compressed in order to increase the filling density, the active

carbon hexagonal mesh surface edge which is not covered with amorphous carbon is exposed, deterioration of the charge and discharge efficiency due to compression is extremely large.

On the other hand, the flake graphite particles have a small friction coefficient, which is preferable for increasing the filling density. However, when only the flake graphite particles are used as the negative electrode active material, the graphite particles are uniformly oriented by pressure compression. Which leads to degradation of the wettability of the electrode and the electrolyte solution. Therefore, the negative electrode hardly impregnates with the electrolyte solution, and the coefficient of effective utilization is hence decreased, thereby reducing the capacity of the battery.

As a countermeasure, the present invention uses both the graphite material whose surface is covered with amorphous carbon and the flake graphite particles to be mixed. As a result, as compared with the case where the graphite material whose surface is covered with amorphous carbon is solely used, the filling density can be increased with a smaller pressure, and it is possible to suppress deterioration of the battery properties due to fracture of the graphite particles whose surfaces are covered with amorphous carbon. Since the flake graphite particles have a small friction coefficient (it can be considered that they function as cushions because they are squashy), the friction resistance between the graphite material particles whose surfaces

are covered with amorphous carbon becomes small, and whereby the particles are apt to be shifted from each other during compression, increasing the filling properties. Therefore, the negative electrode according to the present invention can sufficiently
5 increase the density with a small pressure, and fracture of the graphite particles whose surfaces are covered with amorphous carbon can be suppressed.

Since it is possible to absorb the uniform orientation of the flake graphite particles during pressure compression,
10 appropriate irregularities can be formed on the surface of the negative electrode. Therefore, the negative electrode according to the present invention is superior in the wettability to the electrolyte solution, as compared with the negative electrode using only the flake graphite particles as the negative electrode
15 active material.

Therefore, according to the present invention, it is possible to obtain a high-performance nonaqueous electrolyte secondary battery which exerts a high charge and discharge efficiency.

20

[Mode for Carrying Out the Invention]

As a method for obtaining a graphite material whose surface is covered with amorphous carbon used in the present invention, there is a method including a step of mixing a graphite
25 material such as natural graphite or artificial graphite using

petroleum pitch or coal pitch as a raw material and a petroleum pitch or coal tar pitch and a step of calcining at 2500 to 3000° C. Alternately, the graphite material whose surface is covered with amorphous carbon can be similarly obtained by thermally decomposing fused hydrocarbon such as benzene or xylene by the CVD method to deposit on the surface of the graphite material.

Additionally, as a most preferable graphite material whose surface is covered with amorphous carbon for use in the present invention, there is a material which is obtained by graphitizing mesocarbon microbeads (mesophase pitch based carbon microbeads) at 2500 to 3000°C. The mesocarbon microbeads can be obtained by subjecting coal tar pitch and the like to heat treatment at a temperature of approximately 350 to 450°C, separating the generated spherulite by a method such as centrifugation and cleaning it by using a solvent such as toluene or xylene. The ground substance content such as pitch remains on the surface of the mesocarbon microbeads. After carbonizing this at approximately 800 to 1500°C, it is calcined at 2500 to 3000°C. During this calcination, the ground substance content such as pitch on the surface becomes amorphous carbon, and the internal mesocarbon microbeads become the graphite material having the high crystallinity. In the case of such a material, since amorphous carbon coat can be naturally generated in the manufacturing process, the afore-mentioned coat generation process can be omitted.

As the specific surface area of the graphite material whose surface is covered with amorphous carbon, 0.3 m²/g to 3 m²/g is preferable. When the specific surface area is smaller than 3 m²/g, decomposition of the electrolyte solution can be sufficiently suppressed, thereby further improving the charge and discharge efficiency. In addition, when the specific surface area is set equal to or larger than 0.3 m²/g, the sufficiently high rate properties (i.e., reduction in the capacity is small even if the current for charge and discharge is increased) can be readily obtained. In particular, 0.5 m²/g to 1 m²/g is more preferable.

The examples of the flake graphite particles for use in the present invention include graphite particles obtained by heat-treating at a high temperature of not less than 2500°C an easily graphitizable material obtained from petroleum pitch coke or coal pitch coke, and natural graphites produced in China and Madagascar. In particular, since artificial graphite obtained by graphitizing needle coke or fluid coke using petroleum pitch or coal pitch as a raw material has a smaller amount of impurities than the natural graphite, the former is desirably superior in the charge and discharge efficiency.

Each flake graphite particle has a plane portion and a side surface portion and is definitely distinguished from the graphite particle having any other shape, e.g., granulated, aggregated, fiber type or fish scale-like graphite particle.

Furthermore, in the flake graphite particles for use in the present invention, the shape of the primary particles should be flake, and the particles may be in the form of the secondary particles.

Moreover, as the weight average particle diameter, 10
5 μm to 80 μm is preferable. The particle diameter in this case has a value obtained by the laser diffraction method. When the weight average particle diameter is not more than 80 μm , the effect for improving the filling properties can be sufficiently obtained, thereby increasing the negative electrode density. In addition,
10 when the weight average particle diameter is not less than 10 μm , the specific surface ratio does not excessively become larger, which does not lead to the deteriorated charge and discharge efficiency.

In the present invention, a blend ratio between the
15 graphite material whose surface is covered with amorphous carbon and the flake graphite particles is important. Additionally, the amount of the flake graphite particles are preferably in a range of 10 to 70 wt% of the total weight of the negative electrode carbon material (however, the total weight means a sum total of
20 the both materials if the carbon material consists of only the graphite material whose surface is covered with amorphous carbon and the flake graphite particles), and particularly preferably 20 to 45 wt%.

Since the effect for improving the filling properties
25 can be sufficiently obtained with a blend ratio of not less than

10 wt%, the energy density of the battery can be increased. When the blend ratio is not more than 70 wt%, the wettability of the electrode and the electrolyte solution can be prominently improved, and the coefficient of effective utilization of the active
5 material can be increased, thereby enlarging the capacity of the battery.

The carbon material for use in the present invention can contain any other carbon material than the graphite material having the surface covered with amorphous carbon and the flake
10 graphite particles, and a carbon material such as acetylene black which can be typically used as a conductivity enhancing material may be contained. In this case, any other carbon material preferably corresponds to 3% or less of all the negative carbon materials.

15 In order to form the negative electrode used in the present invention, a usual method can be used. Predetermined amounts of the graphite material having the surface covered with amorphous carbon and the flake graphite particles are mixed with a later-described binder in an appropriate dispersion solvent. The
20 obtained slurry is applied onto a current collector, the solvent is dried, and the resultant layer is then compressed and molded by using an adequate press machine.

The present invention can adopt a relatively low pressure as a press pressure. It is possible to sufficiently attain 1.3
25 to 1.8 (g/cc) which is the usually required filling density with

a pressure smaller than a necessary pressure in the prior art (more than 8 ton/cm² and equal to approximately 10 ton/cm²). It is sufficient to use even a pressure less than 3 ton/cm² depending on a content of the flake graphite.

5 As a positive electrode for use in the present invention which permits doping with lithium ions and de-doping, a lithium containing composite oxide is preferable. There are, for example, LiCoO₂, LiNiO₂, LiMn₂O₄, LiFeO₂, and others or those obtained by replacing part of these Co, Ni, Mn and Fe with other metal elements.

10 Examples of an organic solvent for the electrolyte solution for use in the present invention include ethers, ketones, lactones, sulfolane-based compounds, esters and carbonates. Typical examples of these materials include tetrahydrofuran, 2-methyl-tetrahydrofuran, γ -butyl lactone, acetonitrile,
15 dimethoxyethane, diethyl carbonate, propylene carbonate, ethylene carbonate, dimethyl sulfoxide, sulfolane, 3-methyl-sulfolane, ethyl acetate, methyl propionate and mixed solvents of these materials.

20 No particular restriction is put on the electrolyte salt for use in the present invention, but usable are LiBF₄, LiAsF₆, LiPF₆, LiClO₄, CF₃SO₃Li and the like. Among these, LiBF₄, LiClO₄, LiPF₆ and the like are preferable in view of the battery properties, handling safety and others.

25 As a current collector, a metal foil such as a copper foil, a carbon sheet or a metal mesh can be used.

No particular restriction is put on a binder which can be used for binding the electrode material to the current collector, but usable are polytetrafluoroethylene, polyethylene, nitrile rubber, polybutadiene, butyl-rubber, polystyrene, styrene/butadiene rubber, nitrocellulose, cyanoethyl cellulose, and polymers of vinyl fluoride or vinylidene fluoride and the like. Although an amount of the binder is not restricted, it is within a range of 0.1 to 20 wt%, more preferably 3 to 15 wt% with respect to 100 wt% of the active material.

No particular restriction is put on the separator, but for example, a single sheet of fine porous film of a polyolefin such as polyethylene or polypropylene, or a laminate sheet of such films can be used.

Although the shape of the battery is not particularly restricted, there can be selected, e.g., a cylindrical, an angular or a coin-like shape.

[Examples]

The present invention will now be described in detail on the basis of examples and comparative examples, the scope of the present invention should not be restricted thereto.

A material (HAG-5P) obtained by mixing artificial graphite (HAG-5) manufactured by Nihon Kokuen Co., Ltd. with petroleum pitch and heat-treating the mixture at 2800°C was used as a graphite material having the surface covered with amorphous

carbon. Natural graphite (NG-15) manufactured by Kansai Netsukagaku Co., Ltd. was used as flake graphite particles. With these material a negative electrode was produced. When the specific surface area of HAG-5P was measured by a B.E.T. method using a Quantasorb manufactured by Quantachrome Corp., a value of 3.7 m²/g was obtained. Nitrogen was used as absorption gas, and the carbon material was heated in the nitrogen atmosphere at 150°C before measurement to remove the adsorbates on the surface.

When the size distribution of NG-15 was measured by the laser diffraction method using an automatic size distribution measuring device manufacturing by Horiba, the weight average particle diameter was 14.7 μm.

HAG-5P and NG-15 were mixed at a mixture ratio such as shown in Table 1 and used as a negative electrode active material. 12 wt% of the polyvinylidene fluoride manufactured by Kureha Chemical Industry Co., Ltd. was added to this carbon material to be used as a negative electrode material. This negative electrode material was dispersed in the N-methyl-2-pyrrolidone to obtain a slurry, and the obtained slurry was applied on a copper foil and then dried. The thus treated foil was further compressed by a uniaxial press machine to regulate a filling density to not less than 1.45 g/cc, thereby obtaining a negative electrode sheet.

The surface area of the negative electrode sheet was measured by the B.E.T. method using a Quantasorb manufactured by Quantachrome Corp. Table 1 shows the filling density and the

specific surface area of each negative electrode after pressure formation and the pressure of the uniaxial press. Here, the filling density of the negative electrode means the apparent density of only the negative electrode mixture from which the copper foil as a current collector is removed. The negative electrode filling density can be readily obtained by measuring the weight and the thickness of an electrode having an arbitrary area and subtracting a value of the copper film as the current collector from the measurement value. Also, the specific surface area of the negative electrode means a value obtained by dividing the surface area of the negative electrode sheet measured by the above-described method by the weight of the negative electrode from which the current collector is removed.

Based on Table 1, it is understood that the pressure required for obtaining the filling density of the negative electrode which is not less than 45 g/cc is suddenly decreased when an amount of the flake graphite particles (NG-15) becomes not less than 10 wt%. It is also found that the specific surface area of the negative electrode after pressure compression becomes minimum when an amount of the flake graphite particles is 30 wt%.

Table 1

Negative Electrode Number	HAG-5P/NG-15	Negative Electrode Filling Density (g/cc)	Pressing Pressure (ton/cm ²)	Specific Surface Area of Negative Electrode (cm ² /g)
1	95/5	1.46	8.0	4.1
2	90/10	1.47	4.5	3.4
3	70/30	1.50	3.4	2.1
4	50/50	1.49	3.0	2.6
5	30/70	1.50	2.1	3.1
6	10/90	1.52	1.8	3.5

<Examples 1 to 6>

5 Coin type nonaqueous electrolyte solution secondary batteries were prepared by using negative electrodes of negative electrode numbers 1 to 6 as Examples 1 to 6. The respective example numbers and negative electrode numbers used therefor correspond to each other. To obtain a positive electrode, Lithium cobaltate (LiCoO₂) was mixed with 5 wt% of polyvinylidene fluoride
10 manufactured by Kureha Chemical Industry Co., Ltd., 1 wt% of acetylene black and 4 wt% of artificial graphite SP8 manufactured by Nihon Kokuen Co., Ltd., and the resultant mixture was then dispersed in N-methyl-2-pyrrolidone to obtain a slurry. This
15 slurry was applied onto an aluminum foil and then dried, and the resultant layer was further compressed by a uniaxial press machine to obtain a positive electrode.

 A mixed solvent (a mixing volume ratio: EC/PC/DMC = 20/20/60) of ethylene carbonate (EC), propylene carbonate (PC)
20 and dimethyl carbonate (DMC) in which LiClO₄ having a concentration

of 1 mole/liter was dissolved was used as an electrolyte solution.
A polypropylene non-woven fabric was used as a separator.

These constituent materials were used to produce the
nonaqueous electrolyte secondary battery consisting of a positive
5 electrode case 1, a negative electrode case 2, a negative electrode
current collector 3, a negative electrode active material 4, a
separator 5, a gasket 6, a positive electrode current collector
7 and a positive electrode active material 8, as shown in a
cross-sectional view of Fig. 1.

10 The battery charge and discharge properties were measured
as follows. That is, the discharge properties were measured in
a low-current charge and discharge of 0.1 mA/cm². After charging
up to 4.2 V, discharge was carried out to 3 V. A discharge capacity
was determined as a capacity per a negative electrode active
15 material when a cutoff voltage became 3 V. In addition, a charge
and discharge efficiency was shown as a ratio of the discharge
capacity to the charge capacity in the first cycle. The results
are shown in Table 2.

<Comparative Example 1>

20 The same procedure as in the preparation of negative
electrode numbers 1 to 6 was conducted except that HAG-5P alone
was used as a negative electrode active material, and pressed
under a pressing pressure of 8.2 (ton/cm²) to obtain a negative
electrode having a negative electrode filling density of 1.45
25 g/cc (g/cc) and a negative electrode specific surface area of

5.8 (cm²/g). The same procedure as in Example 1 was carried out using this negative electrode, thereby preparing a coin type nonaqueous electrolyte secondary battery, and its charge and discharge properties were then measured. The results are shown in Table 2.

<Comparative Example 2>

The same procedure as in the preparation of negative electrode numbers 1 to 6 was conducted except that NG-15 alone was used as a negative electrode active material, and pressed under a pressing pressure of 1.0 (ton/cm²) to obtain a negative electrode having a negative electrode filling density of 1.48 g/cc (g/cc) and a negative electrode specific surface area of 6.3 (cm²/g). The same procedure as in Example 1 was carried out using this negative electrode, thereby preparing a coin type nonaqueous electrolyte secondary battery, and its charge and discharge properties were then measured. The results are shown in Table 2.

Table 2

	Negative Electrode Number	Charge and Discharge Efficiency	Discharge Capacity (mAh/g)
Example 1	1	0.74	228
Example 2	2	0.82	258
Example 3	3	0.87	305
Example 4	4	0.85	307
Example 5	5	0.81	303
Example 6	6	0.71	271
Comparative Example 1	Only HAG-5P	0.65	212
Comparative Example 2	Only NG-15	0.56	180

As apparent from Table 2, in the examples according to
 5 the present invention, it is possible to obtain the
 high-performance nonaqueous electrolyte secondary battery which
 exerts a charge and discharge efficiency of not less than 0.70
 and a discharge capacity of not less than 220 mAh/g even if the
 negative electrode filling density is not less than 1.45 g/cc.
 10 Particularly, in Examples 2 to 5 in which the mixing ratio of
 NG-15 is within a range of 10 to 70% of the entire negative electrode
 carbon in terms of the weight ratio, it is possible to obtain
 the high-performance nonaqueous electrolyte secondary battery
 which exerts a charge and discharge efficiency of not less than
 15 0.80 and a discharge capacity of not less than 250 mAh/g.

<Example 7>

A material obtained by graphitizing mesocarbon
 microbeads (MCMB30-28, manufactured by Osaka Gas Co., Ltd.,

specific surface area = $0.98 \text{ m}^2/\text{g}$) was used as a graphite material whose surface was covered with amorphous carbon, and artificial graphite (SFG75, manufactured by Lonza Co., Ltd., average particle diameter = $34.3 \text{ }\mu\text{m}$) obtained from coal pitch as a raw material was used as flake graphite particles. MCMB30-28 and SFG75 were mixed so that a ratio of MCMB30-28 in a negative electrode carbon material might be 75 wt% and a ratio of SFG75 in the same might be 25 wt% of the total, thereby obtaining a negative electrode active material.

The same procedure as in Example 1 was conducted using this negative electrode active material to form a negative electrode. A filling density of the negative electrode was regulated to not less than 1.6 g/cc by the use of a uniaxial press. A pressing pressure of $2.6 \text{ (ton/cm}^2\text{)}$ was used to obtain a negative electrode having a negative electrode filling density of 1.64 (g/cc) and a negative electrode specific surface area of $1.7 \text{ (cm}^2/\text{g)}$.

To obtain a positive electrode, LiMn_2O_4 was mixed with 5 wt% of polyvinylidene fluoride manufactured by Kureha Chemical Industry Co., Ltd., 1 wt% of acetylene black and 4 wt% of artificial graphite SP8 manufactured by Nihon Kokuen Co., Ltd., and the resultant mixture was then dispersed in N-methyl-2-pyrrolidone to obtain a slurry. This slurry was applied onto an aluminum foil and then dried, and the resultant layer was further compressed by a uniaxial press machine to obtain a positive electrode.

A mixed solvent (a mixing volume ratio: EC/DEC = 45/55) of ethylene carbonate (EC) and diethyl carbonate (DEC) in which LiClO_4 having a concentration of 1 mole/liter was dissolved was used as an electrolyte solution. A polypropylene non-woven fabric was used as a separator. A coin type electrolyte secondary battery was prepared by using these materials, and its battery properties were then measured in the same manner as in Example 1. The results are shown in Table 3.

<Example 8>

As in Example 7, a material obtained by graphitizing mesocarbon microbeads (MCMB3-28, manufactured by Osaka Gas Co., Ltd., specific surface area = $4.62 \text{ m}^2/\text{g}$) was used as a graphite material whose surface was covered with amorphous carbon, and artificial graphite (SFG75, manufactured by Lonza Co., Ltd., average particle diameter = $27.3 \mu\text{m}$) prepared from coal pitch as a raw material was used as flake graphite particles. MCMB3-28 and SFG75 were mixed so that a ratio of MCMB3-28 might be 75 wt% and a ratio of SFG75 might be 25 wt% of all the negative electrode carbon materials, thereby obtaining a negative electrode active material. As in Example 7, this negative electrode active material was used under a pressing pressure of $2.4 \text{ (ton/cm}^2\text{)}$ to obtain a negative electrode having a negative electrode filling density of 1.66 (g/cc) and a negative electrode specific surface area of $2.3 \text{ (cm}^2/\text{g)}$. As in Example 7, a coin type nonaqueous electrolyte secondary battery was prepared, and its battery

properties were then measured. The results are shown in Table 3.

<Example 9>

As in Example 7, a material obtained by graphitizing
5 mesocarbon microbeads (MCMB30-28, manufactured by Osaka Gas Co.,
Ltd., specific surface area = $0.98 \text{ m}^2/\text{g}$) was used as a graphite
material whose surface was covered with amorphous carbon, and
artificial graphite (SFG15, manufactured by Lonza Co., Ltd.,
average particle diameter = $6.1 \text{ }\mu\text{m}$) prepared from coal pitch as
10 a raw material was used as flake graphite particles. MCMB30-28
and SFG6 were mixed so that a ratio of MCMB30-28 might be 75 wt%
and a ratio of SFG15 might be 25 wt% of all the negative electrode
carbon materials to obtain a negative electrode active material.
The same procedure as in Example 7 was carried out except for
15 the above requirements to prepare a coin type nonaqueous
electrolyte secondary battery. As in Example 7, this negative
electrode active material was used under a pressing pressure of
 $2.4 \text{ (ton/cm}^2\text{)}$ to obtain a negative electrode having a negative
electrode filling density of 1.62 (g/cc) and a negative electrode
20 specific surface area of $2.2 \text{ (cm}^2/\text{g)}$. As in Example 7, the coin
type nonaqueous electrolyte secondary battery was prepared, and
its battery properties were then measured. The results are shown
in Table 3.

<Comparative Example 3>

25 The same procedure as in Example 7 was conducted except

that graphitized MCMB3-28 alone was used as a negative electrode active material, thereby preparing a coin type nonaqueous electrolyte secondary battery, and its battery properties were then measured. The results are shown in Table 3. However, a pressing pressure in the preparation of a negative electrode was 2.4 (ton/cm²). In the thus prepared battery, a negative electrode filling density was 1.62 (g/cc) and a negative electrode specific surface area was 2.2 (cm²/g).

<Comparative Example 4>

10 The same procedure as in Example 7 was conducted except that SFG15 alone was used as a negative electrode active material, thereby preparing a coin type nonaqueous electrolyte secondary battery, and its battery properties were then measured. The results are shown in Table 3. However, a pressing pressure in the preparation of a negative electrode was 1.5 (ton/cm²). In the thus prepared battery, a negative electrode filling density was 1.61 (g/cc) and a negative electrode specific surface area was 2.8 (cm²/g).

Table 3

	Charge and Discharge Efficiency	Discharge Capacity (mAh/g)	Negative Electrode Filling Density (g/cc)
Example 7	0.93	335	1.64
Example 8	0.83	296	1.66
Example 9	0.81	311	1.62
Comparative Example 3	0.67	265	1.61
Comparative Example 4	0.63	220	1.61

As apparent from Table 3, the battery according to
 5 Examples 7 and 8 in which the material obtained by graphitizing
 mesocarbon microbeads was used as the graphite material having
 the surface covered with amorphous carbon and the artificial
 graphite having coal pitch as a raw material was used as the flake
 graphite particles shows a excellent performance such as a charge
 10 and discharge efficiency of not less than 0.80 and a discharge
 capacity of not less than 290 mAh/g even if the negative electrode
 density is not less than 1.6 g/cc.

In particular, the battery according to example 7 in which
 the specific surface area of the graphite material having the
 15 surface covered with amorphous carbon is within a range of 0.3
 m^2/g to 3 m^2/g and the average particle diameter of the flake
 graphite particles is within a range of 10 μm to 80 μm exerts
 an excellent performance such as a charge and discharge efficiency
 of not less than 0.90 and a discharge capacity of not less than
 20 320 mAh/g.

[Effect of the Invention]

According to the present invention, it is possible to provide the nonaqueous electrolyte secondary battery having the high capacity and the excellent charge and discharge efficiency.

5

[BRIEF DESCRIPTION OF THE DRAWINGS]

Fig. 1 is a cross-sectional view showing an embodiment of a nonaqueous electrolyte secondary battery according to the present invention.

10 [Explanation of symbols]

- 1: Positive electrode case
- 2: Negative electrode case
- 3: Negative electrode current collector
- 4: Negative electrode active material
- 5: Separator
- 6: Gasket
- 7: Positive electrode current collector
- 8: Positive electrode active material

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[Name of Document] Drawing

[Fig. 1]

